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Art. XII.—*The Thermal Conductivity of Carbon Dioxide between* 78·50°*C.* *and* 100°*C.*

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According to the kinetic theory, the thermal conductivity of a gas should increase with the temperature. Although this prediction is generally confirmed by experiment, it is impossible to deduce from the existing experimental data any more specific conclusions. According to Loeb (Kinetic Theory of Gases, p. 251) "the results of the many experiments are none the less quite discordant and little can be deduced from them." On the other hand, the absolute values at 0°C. of the conductivities of some of the commoner gases are known with reasonable accuracy, and so it can be concluded that experimental procedures which lead to tolerably accurate values of the conductivity at 0°C. are either inapplicable or unsuited to investigations carried out at other temperatures. In the present paper an account will be given of some preliminary experiments undertaken to investigate the temperature variation of the conductivity of carbon dioxide gas. The method used is one that was developed twelve years ago, and was applied successfully to determine the conductivity of a number of gases at 0°C.(1). In those experiments a hot wire method was used in which the wire was relatively short and thick, instead of long and fine as in the older traditional forms of the hot wire method. It would seem that the short thick wire offers greater prospects of success in a rather difficult field of investigation.

A short account of the two types of hot wire experiment will first be given. In all hot wire experiments a metal wire, which is heated by passing an electric current through it, is mounted axially in a glass or metal tube which contains the gas under investigation and which is immersed in a constant temperature bath. The wire serves both as a resistance thermometer and as a heater of the gas in the tube. The average rise in temperature of the wire on passing a given current through it will depend on the conductivity of the gas surrounding the wire. The hot wire method depends on this fact, but carries with it the obligation of completely eliminating convection currents in the gas. This problem was studied experimentally by Sophus Weber(2) and it is now possible to design and set up an apparatus in such a way that convection currents are completely absent. Three conditions which must be satisfied are (1) that the tube be mounted vertically, (2) that it is not too wide, and (3) that the temperature difference between the wire and the tube be kept small.

A difficulty which is met with to a greater or less extent in all hot wire experiments has its origin in the existence of a discontinuity of temperature at any solid-gas interface. The steeper the temperature gradient near the surface, the greater the temperature discontinuity or drop. The prevalent use of fine wires greatly aggravates the difficulty, the temperature gradient at the surface being much steeper for thin than for thick wires. The magnitude of the temperature drop increases with the mean free path of the molecules, i.e., with decreasing pressure of the gas. By making use of this fact it is possible to correct a set of values of the conductivity obtained at different pressures for the effect of the temperature drop.

The different kinds of hot wire apparatus being always symmetrically constructed, the distribution of the temperature along the wire is also symmetrical with respect to the two ends of the wire. When the wire is sufficiently long and fine the graph of the temperature along the wire is shaped very like a top hat, i.e., there is a central portion of the wire along which the temperature is constant. The length of this portion is relatively greater the longer the wire is and the smaller its diameter. As there is no temperature gradient anywhere in this part of the wire all the Joule heat developed in it by the electric current must be carried away laterally from the surface of the wire by conduction through the gas and by radiation (assuming, of course, convection is absent). If the wire is uniform and has a truly circular cross-section and if it be mounted along the axis of a truly cylindrical tube the flow of heat by conduction through the gas from the portion of wire at constant temperature is radial and takes place between concentric cylindrical surfaces defined by the wire surface and the inner surface of the tube. If this particular portion of the wire can be isolated so that the measurements are made with respect to it and not the whole wire, the theory of the experiment takes on a very simple character.

The isolation can be effected in either of two ways. In one of these due to Schleiermacher (1888)[(3)] the central portion is tapped by introducing two potential leads of very fine wire through the wall of the tube and attaching them to the wire at appropriate points. In the other, devised by Goldschmidt (1911)[(4)] two tubes are employed which are identical in all respects except that one is short and the other long. The wire in the shorter tube plays a similar role to that of the compensating leads of the platinum thermometer. The difference in the electrical resistance of the long and short tube will give the resistance of the central portion of the wire from which the flow of heat is radial.

Let h be called the external conductivity, defined as the loss of heat per second from unit area of the wire surface per degree difference of temperature between the wire and the tube. Then, if l be the length of the central portion and b the radius of the wire, the rate at which heat is lost from the surface is:

$$2\pi blh\ (t_1 - t_2)$$

where t_1 is the temperature of the wire obtained indirectly from resistance measurements, and t_2 is that of the tube. The rate at which Joule heat is developed in the part of the wire under consideration is RI^2/J, where R ohm is its resistance when the current is I ampere. Since no heat is conducted along the wire it follows that:

$$2\pi blh\ (t_1 - t_2) = RI^2/J \qquad (1)$$

where $J = 4{\cdot}18$ joule/cal.

All the quantities in this equation are either known or can be measured, except h, which can therefore be determined. If the loss of heat from the wire by radiation is inappreciable compared with the loss by conduction the thermal conductivity k of the gas can be obtained by multiplying h by a certain " form factor ", the value of which is determined by the fact that the flow of heat is radial and takes place between concentric cylindrical surfaces. The appropriate form factor can be shown to be $b \log_e a/b$, a being the inner radius of the tube, and b the radius of the wire. Accordingly we write:

$$k = h.b \log_e a/b \qquad (2)$$

The type of hot wire experiment just described has a number of unfavourable features. Whichever of the two methods is used for isolating the constant temperature part of the wire, an inconveniently long apparatus results. For this reason such an apparatus is unsuitable when measurements of the conductivity over a range of temperature are required. The diameters of the hot wires used are quite small (usually a few thousandths of an inch only) and cannot be determined as accurately as those of thick wires. In some investigations merely an average diameter of the wire is obtained by weighing in air and in water a known long length of the wire used. As the temperature gradient at the surface of such fine wires is very great, the wire should be uniform and accurately circular in section. These are requirements which can be verified only by contact measurements.

The above type of hot wire experiment was devised before modern high vacuum technique was developed. The use of the short thick hot wire is made to depend upon the fact that, when a sufficiently high vacuum is produced in the tube, all the Joule heat generated by the electric current is conducted out of the ends of the wire and none is lost laterally, except a very small amount by radiation which can be allowed for by calculation. Thus an experiment performed when the tube is highly evacuated leads to a determination of the thermal conductivity of the wire itself. It is clear that in this kind of hot wire experiment, when the tube contains a gas, some heat is conducted along the wire and some is also lost laterally. The theory is necessarily less simple, but the gains on the experimental side are so great as to more than compensate for its use.

The following simplified account of the theory is sufficient to illustrate the principles of the method. For calculating the conductivity it is, however, necessary to use the more accurate theory given in the Appendix to this paper.

For a short thick wire of radius b mounted axially in a tube maintained (say) at 0°C. the distribution of temperature along the wire can be shown to be very nearly parabolic. Accordingly, if the centre of the wire (length 2l) be taken as origin, the temperature at any point on it distant x from the centre will be given by:

$$t = c\,(l^2 - x^2) \qquad (3)$$

c being a constant (see fig. 1).

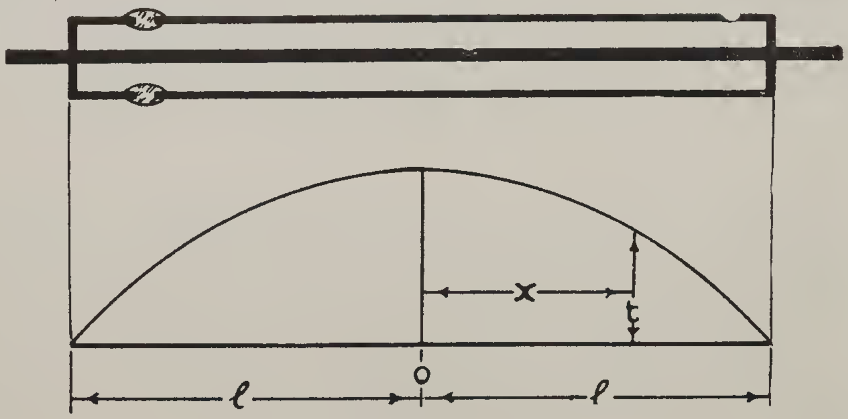

Fig. 1.

Clearly the temperature has a maximum value of cl^2 at the middle and it is zero at both ends.

The mean temperature of the wire can easily be shown to be: $\bar{t} = 2cl^2/3$.

$$\left(\bar{t} = \frac{1}{2l} \int_{-l}^{+l} c(l^2 - x^2)\, dx = 2cl^2/3\right)$$

The temperature gradient at any point in the wire is, by (3):

$$\frac{dt}{dx} = -2cx$$

At either end the gradient is therefore:

$$\left(\frac{dt}{dx}\right)_{x=+l} = -2cl = -\frac{3\bar{t}}{l}$$

The rate at which heat is conducted out of the wire at the two ends is:

$$2\left(-\lambda A\left(\frac{dt}{dx}\right)_{x=+l}\right) = \frac{6\lambda\pi b^2 \bar{t}}{l}$$

λ being the thermal conductivity of the wire, and $A = \pi b^2$ its cross-section.

The rate at which heat is lost from the surface of the wire is:

$$2\pi b \,.\, 2l \,.\, \bar{t} \,.\, h = 4\pi b\, l\, h\, \bar{t}$$

where h is the external conductivity.

The rate at which heat is generated in the wire by the electric current is $\bar{R}I^2/J$ where $\bar{R}$ is the resistance of the wire when the current is I ampere. The sum of the heat lost per second by internal conduction and by external conduction must equal the joule heat produced per second by the current. Accordingly we have:

$$\frac{6\lambda\pi b^2}{l}\bar{t} + 4\pi l\, b\, h\, \bar{t} = \frac{\bar{R}I^2}{J} \qquad (4)$$

If α be the temperature coefficient of the resistance, then for a small rise of temperature:

$$\bar{R} = R_0(1 + \alpha\bar{t})$$

where R_0 is the resistance of the wire at 0°C. Solving for $\bar{t}$ we obtain:

$$\bar{t} = \frac{\bar{R} - R_0}{R^0\alpha}$$

and substitution of this value of $\bar{t}$ in (4) gives:

$$\frac{6\lambda\pi b^2(\bar{R} - R_0)}{R_0\alpha l} + \frac{4\pi bhl(\bar{R} - R_0)}{R_0\alpha} = \frac{\bar{R}I^2}{J}$$

or

$$\frac{h}{b} = \frac{R_0\bar{R}I^2\alpha}{4(\bar{R} - R_0)\pi b^2 Jl} - \frac{3\lambda}{2l^2} \qquad (5)$$

For the special case in which there is a high vacuum in the tube we may put h = 0 in (5) and so obtain Knudsen's formula:

$$\lambda = \frac{1}{6} \frac{\bar{R} R_0 I^2 \alpha l}{J \pi b^2 (\bar{R} - R_0)} \qquad (6)$$

Knudsen proved that it was possible to measure the thermal conductivity of a metal accurately by means of (6), using a platinum wire a couple of centimetres in length and a few tenths of a millimetre in diameter. The conductivity of the wire having been determined by (6), the value of λ is next introduced into (5), which equation may then be solved for h and the conductivity of the gas is obtained, as in the other method, through (2). The form factor b $\log_e$ a/b is an approximation as the flow of heat by conduction through the gas is not strictly radial. The error introduced into k by its use can be proved to be less than 1 per cent. It follows that the accuracy with which the conductivity of a gas can be obtained by this method depends upon the accuracy with which the conductivity of the wire is obtained. It will be noticed that if the current is kept constant the only quantity which has different values in (5) and (6) is $(\bar{R}-R_0)$, and that for a given current $(\bar{R}-R_0)$ necessarily has its maximum value in (6), i.e., under high vacuum conditions, and here optimum accuracy in its measurement is most desirable.

The method described has, in the earlier work[1], been submitted to searching tests, by varying all the factors upon which the conductivity of a gas depends. Wires and tubes of different materials and dimensions have been tried. Both platinum and copper wires were employed, and although the thermal conductivity of copper is six times that of platinum, practically identical values of the conductivity of air, as also of hydrogen gas, were obtained.

Description of the Apparatus

In order to investigate the conductivity at fixed temperatures other than the ice point, a small and compact conductivity apparatus is essential if accurate temperature control is to be achieved. One form of the apparatus used in the earlier work at the ice point was judged suitable for measurements of the conductivity at the steam point (100°C.), the ice point (0°C.), the carbon-dioxide point (—78·50°C.), and the oxygen point (—183°C.). This apparatus consisted of a platinum wire 1·5 mm. in diameter mounted in a stainless steel tube 10 cm. long, and having an internal diameter of 12 mm. Some preliminary tests made with this apparatus (which had been out of use for twelve years) indicated that some deterioration in the soft solder used in fixing the wire in the tube had occurred. It was therefore decided to dismantle the apparatus and re-assemble it using silver solder wherever soldering was necessary. The inner surface of the tube was re-lapped and a new copper-glass seal was made. The platinum wire was re-drawn using diamond dies and then carefully annealed at 950° in a muffle furnace. A recently-calibrated set of slip gauges was used in conjunction with micrometer screw gauges and a pair of internal jaws to determine the dimensions of the tube and wire, and the tube was then re-assembled. Fig. 2 is a sketch of the completed apparatus. The wire is insulated electrically from the steel tube by means of a double glass copper join G in the lower copper end-cap C. The tube is closed at either end by a thin copper end-cap, about 1 mm. thick, through the centre of which the wire is soldered. The side tube T is sealed to a wider glass tube leading off to a vacuum pump, a simple U-tube mercury manometer, a discharge tube, and a tap through which gas may be introduced. The current and potential leads immediately above the tube were wrapped in cotton wool to protect them from draughts, which, particularly in steam point determinations, had produced fluctuations in current and potential readings.

FIG. 2.

In order to measure the thermal conductivity of a gas, the apparatus is pumped out through one tap and the pure gas is then introduced through another until its pressure in the apparatuus is approximately atmospheric pressure. The gas is later pumped off a little at a time in order to enable readings at various pressures to be taken.

When a determination of the thermal conductivity λ of the wire is to be made, the mercury manometer is removed and a tube containing activated charcoal is substituted for it. The high vacuum required is obtained in the usual way by immersing the charcoal tube in liquid air after degassing the charcoal.

DIMENSIONS OF TUBE AND WIRE AT 0°C.

Mean distance between the internal faces of the copper end-caps (i.e., effective length of the platinum wire) = 103·87 mm. ± ·05 mm.

Mean internal diameter of steel tube
= 12·814 mm. ± ·005 mm.

Mean diameter of platinum wire
= 1·438 mm. ± ·003 mm.

MEASUREMENT OF ELECTRICAL QUANTITIES.

Apart from the dimensions of the wire and the tube, the other quantities required are electrical ones, viz.: R_0, the resistance of the wire at the temperatures of the constant temperature bath in which the apparatus is immersed; a, the temperature coefficient of the resistance at that temperature; $\overline{R}$, the measured resistance of the wire when it carries a steady current of I amperes.

Of these, R_0 and a are electrical constants which are both obtained indirectly from measurements of $\overline{R}$.

The quantities $\overline{R}$ and I are obtained directly by comparing the drop of potential across the wire with the drop across a standard ·01 ohm resistance by Tinsley. A five-dial Diesselhorst low-resistance potentiometer made by Wolff, is used to measure the potential drops. Although the circuit used is a very simple one, great care must be taken in setting it up in order to obtain electrical stability. The work is carried out in a room in which the temperature remains approximately constant near 20°C., the resistances of the coils of the potentiometer being correct at this temperature.

It is not convenient to measure R_0 directly. Instead, a series of values of $\overline{R}$ for different values of I is obtained (whether the tube be evacuated or left filled with a gas is immaterial so long as the conditions inside the tube remain the same during these readings). Corresponding values of $1/\overline{R}$ and I^2 are then plotted upon a large sheet of graph paper. The points so obtained lie very accurately upon a straight line and the line is extrapolated to give $1/R_0$ corresponding to $I = 0$. The value of R_0 actually adopted is obtained by calculation, rather than from the drawn graph, using Cauchy's method (for which see Champion and Davy, Properties of Matter, p. 267).

To obtain α, the variation of the resistance of the platinum wire with the temperature is determined. For platinum it is sufficient to use the two-constant formula:

$$r = (1 + at + bt^2)$$

between $-78 \cdot 50$°C. and 100°C., where $r = R_t/R_0$ 0°C. or the ratio of the resistance at t°C. to the resistance at the ice-point, and a and b are numerical constants. Measurements of the resistance were made at the ice-point, the steam point, and the carbon dioxide point ($-78 \cdot 50$°C.).

The temperature coefficient α at any required temperature t is then given by:

$$= (a + 2bt) \div Rt/R_0 °C.$$

The following figures were obtained:

—	$-78 \cdot 50$°C.	0°C.	100°C.
Resistance (R_0)	·00437978	($R_0$0°c.) ·00639591	·00889862
α	·0059299	·0039705	·0027709
a = ·0039705		b = $-$·000000575	

The above values of a and b lead to the following value of the δ coefficient used in platinum thermometry:

$$\delta = -10^4 \, b/(a + 100b) = 1 \cdot 49$$

Note on the Attainment of the CO_2 Point.

In order to make measurements at the CO_2 point ($-78 \cdot 50$°C.) it was required that the tube be kept at this constant temperature for at least two hours. The tube is nearly 4½ inches long, and is connected by current and potential leads to the rest of the apparatus. When the tube is placed in the CO_2 bath, heat tends to be conducted to the tube from outside along these leads. Moreover, heat is generated in the wire in the tube at the rate of approximately ·07 watt, and this must be dissipated by the bath. The conditions are thus more exacting than is generally the case for ordinary thermometric work.

A separate investigation was required to determine how a dry-ice bath might be used to give satisfactory results. An examination of the literature showed that other workers who had attempted to use this fixed point for thermometric work had experienced difficulty, and apart from a paper by Zeleny and Zeleny[5], little information of any assistance to us was discovered.

The conduction of heat to the tube along the leads was overcome by replacing the lead wires in the vicinity of the tube by thin wide strips of copper which ran parallel with the tube and traversed $5\frac{1}{2}$ inches of the bath before being soldered to the tube. Good thermal contact between the strips or tube and the bath was obtained by using a wet slush of dry-ice chips and ethyl alcohol.

The use of a Dewar flask, as a receptacle for the dry-ice mixture, is not recommended. It was not until its use was abandoned that success in the handling of the bath was obtained.

The tube was placed centrally in a glass gas cylinder, 12 inches tall and $2\frac{1}{2}$ inches in diameter, which stood on $\frac{1}{2}$ inch of felt on a wooden stand. The sides of the cylinder were lagged with two layers (about $1\frac{1}{2}$ inches uncompressed) of cotton wool, which also extended about 2 inches above the top of the jar. A single layer of paper was then tied around the lagging. The dry-ice was reduced to fine chips by means of an ice-grinder, and these chips were mixed with ethyl alcohol in an aluminium saucepan until a wet, but not sloppy, mixture was obtained. This was fed by spoon into the jar surrounding the tube. The mixture in the jar was then prodded with a long thin metal rod to ensure that it was well packed down, and the jar was "topped up" with more wet ice. Finally some alcohol was cooled with dry-ice and added to the jar until about $\frac{1}{4}$ inch of free alcohol remained above the surface of the dry-ice chips.

The tube was left for at least five minutes, at the end of which time a *gentle* bubbling of gas through the surface alcohol could be observed. Thereafter no stirring or prodding was permitted, although the original level and the $\frac{1}{4}$ inch depth of free alcohol were maintained by adding chilled alcohol or wet dry-ice as required.

It was found that such a mixture of dry-ice and alcohol, with free alcohol on top, when lagged with sufficient cotton wool to reduce the evolution of gaseous carbon dioxide to a gentle steady rate, would maintain the tube at the CO_2 point for a period of several hours, and in general, would behave as satisfactorily as an ice-water bath for the $0°C$ point.

It was necessary to apply a correction to allow for the hydrostatic pressure of the alcohol at the point in the bath where the temperature was being measured. In this experiment the hydrostatic pressure at the centre of the tube was calculated, and the temperature of the bath at this depth was taken as the mean temperature of the tube.

Determination of λ.

To determine λ the apparatus is evacuated and a high vacuum ($< 10^{-5}$ mm. of mercury) is produced by means of charcoal and liquid air. The values of $\overline{R}$ corresponding to a series of different values of the current I are obtained and the conductivity, λ, is calculated using formula (6) in the Appendix. (The platinum wire is not sufficiently short to use Knudsen's simpler formula (6) given in the elementary theory.)

RESULTS.

Temperature.	$-78 \cdot 50$°C.	0°C.	100°C.
λ cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$	$\cdot 1603 \pm \cdot 0002$	$\cdot 1675 \pm \cdot 0002$	$\cdot 1690 \pm \cdot 00013$

The value of λ at $-78 \cdot 50$°C. was confirmed by several independent determinations.

DETERMINATION OF k.

The conductivity λ of the wire being known, the apparatus may then be immersed in a constant temperature bath and filled with the gas to be investigated. The current I is set to give a mean rise of temperature of the wire of 3–5 degrees. Corresponding values of $\overline{R}$ and I are then obtained at a series of different pressures of the gas.

The approximate conductivity k′ of the gas is found at each pressure of the gas by solving the equation (4) (or (5)) in the Appendix for h and then k′ is deduced by multiplying h by the form factor b $\log_e$ a/b.

As the flow of heat is not exactly radial (4) or (5) leads to approximate values k′ of the conductivity, but by making use of relations (9) and (8) of the exact theory the amount of the correction to k′ can be worked out. This proves to be quite small, being just under 1 % over a wide range of conductivities. It is sufficient to reduce the conductivity k′ as calculated from (4) (or (5)) by 1% to obtain the value k corrected for the departure from radial flow.

EFFECT OF TEMPERATURE DISCONTINUITY.

On account of the temperature discontinuity at the surface of the wire and at the inner surface of the tube, the space factor for radial flow should be replaced by:

$$b \left[\log_e a/b + \gamma \, (1/a + 1/b) \right] \qquad (6)$$

where γ is related to the temperature discontinuity Δ T by the equation of Poisson:

$$\Delta T = \gamma \frac{dT}{dn}.$$

Here dT/dn is the temperature gradient along the outward drawn normal and γ is a length quantity which varies inversely with the pressure.

It has been found that k at O°C is, in general, constant over a wide range of pressures (60–10 cm. of mercury) for the monatomic and diatomic gases investigated by the apparatus containing the thick platinum wire(1). From these results it is inferred that the effects of convection and of the temperature discontinuity are negligibly small for the range of pressures quoted.

(It should be noted that the effect of reducng the pressure of the gas on its apparent conductivity is to decrease this if convection is present, and also to decrease it on account of the temperature dscontinuity. Consequently, if it is found that k is strictly constant over a range of pressures there can be no convection present and the effect of the temperature discontinuity is likewise negligible.)

The Thermal Conductivity of Carbon Dioxide.

The gas was prepared by heating pure sodium bicarbonate and dried by passing through calcium chloride and phosphorus pentoxide.

The following results were obtained :—

(*a*) At CO_2 Point. Mean Temperature of Gas : —76·4°C.

Pressure (Cm. of Hg.).	Current (I amp.).	$\overline{R} - R_0$ (Ohm).	k′ x 10^5 (−76·4°C.) (cal. cm^{-1} sec^{-1} deg^{-1}).	k x 10^5 (−78·50°C.) (cal. cm^{-1} sec^{-1} deg^{-1}).
77·21	3·69157	·00010037	2·226	2·172
65·01	3·69070	10022	2·236	2·181
55·56	3·69036	10096	2·155	2·102
43·51	3·68985	10115	2·132	2·080
32·96	3·68963	10124	2·122	2·070
22·59	3·68903	10137	2·104	2·053
14·20	3·68864	10160	2·079	2·028
8·24	3·68827	10178	2·060	2·010
3·25	3·68819	10207	2·033	1·983
1·42	3·68766	10220	2·018	1·969
0·23	3·68736	10237	1·996	1·947

In the last column the radial flow correction has been applied and the conductivity reduced to −78·5°C. using a temperature coefficient of ·007.

(*b*) At Ice Point. Mean Temperature of Gas : 2·1°C.

Pressure (Cm of Hg.).	Current (I amp).	$\overline{R} - R_0$ (Ohm).	k′ x 10^5 (2·1°C.) (Cal. cm^{-1} sec^{-1} deg^{-1}).	k′ x 10^5 (0°C.) (Cal. cm^{-1} sec^{-1} deg^{-1}).
67·94	341229	·00010398	3·644	3·569
26·92	340827	10395	3·618	3·544
9·63	340725	10405	3·599	3·525
2·35	340596	10417	3·575	3·501
1·122	340492	10419	3·567	3·494
·854	340387	10413	3·566	3·493
·651	340315	10410	3·564	3·491
·394	340233	10431	3·542	3·469
·271	340166	10451	3·504	3·432

In the last column the radial flow correction has been applied and the conductivity reduced to 0°C. using a temperature coefficient of ·005.

(*c*) At Steam Point. Mean Temperature of Gas : 102·0°C.

Pressure (Cm. of Hg.).	Current (I amp).	$\overline{R} - R_0$ (Ohm).	k′ x 10^5 (102°C.) (Cal. cm^{-1} sec^{-1} deg^{-1}).	k x 10^5 (100°C.) (Cal. cm^{-1} sec^{-1} deg^{-1}).
73·41	2·98103	·00009051	5·705	5·604
39·18	2·98058	9159	5·588	5·489
21·50	2·98000	9170	5·565	5·467
12·21	2·97949	9179	5·546	5·448
4·23	2·97884	9198	5·511	5·414
1·61	2·97829	9243	5·435	5·339

In the last column the radial flow correction has been applied and the conductivity reduced to 100°C. using a temperature coefficient of ·004.

Discussion of Results

These conductivity data for all three temperatures (on account of their gradual decrease with the pressure) are evidently affected by the existence of the temperature discontinuity effect. To allow for this effect the usual procedure is followed of plotting the reciprocal of k against the reciprocal of the pressure p. The plot of points so obtained is straight over a range of pressure in which convection is absent. To obtain the value of k unaffected by the temperature discontinuity the straight portion of the graph is extrapolated to give the value of $1/k$ corresponding to $1/p = 0$. In this way the following values of the thermal conductivity of carbon dioxide are obtained :—

Temperature °C.	−78·50°C.	0°C.	100°C.
$k \times 10^5$ cal. cm^{-1} sec^{-1} deg^{-1}	1·97	3·50	5·46

There is also a second possibility that the observed variation of k with the pressure p is only in part the result of the temperature discontinuity. Ubbelohde[7] has suggested that as the pressure of the gas is reduced the participation of the vibrational energy of the carbon dioxide molecules in the transport of heat becomes less and less complete. This also would result in a decrease in k with the pressure.

Some recent measurements by us on monatomic argon gas show much less variation of k with p. It seems not unlikely that part of the decrease of k with p is concerned with the decrease in the transport of heat by the vibrational energy of the carbon dioxide molecules.

Appendix

Theory of the Method.

The following approximate theory in which the flow of heat from the wire through the ambient gas is assumed to be strictly radial leads to values of the thermal conductvity k′ which are in error by a little less than 1 %. This can be shown to be the case by comparing the values of k as obtained from the approximate theory and from the exact theory which follows later. Accordingly, it is sufficient to use the approximate theory to work out the results and then to apply the small correction which allows for the departure from radial flow.

Approximate Theory.

Let a wire of length 2l and thermal conductivity λ be mounted axially in a tube which is maintained at some constant temperature whch may be taken as an arbitrary zero. Let the annular space between the wire and the tube be filled with a gas of conductivity k.

If the flow of heat from the wire is strictly radial then we have :—

$$\pi b^2 \lambda \frac{d^2t}{dz^2} - 2 \pi b h t + \frac{I^2 R_0(1+\alpha t)}{2lJ} = 0 \quad (1)$$

where R_0 $(1 + \alpha t)$ is the resistance of the wire at t°, R_0 is the resistance at the temperature of the bath in which the apparatus is immersed, and b is the radius of the wire. The first two terms of (1) multiplied by dz represent the net rate of inflow of heat into an element dz along the wire and over its surface, while the last term multiplied by dz is the rate at which heat is produced electrically in the element of length dz. If the following substitutions be made:—

$$\mu^2 = \frac{2h}{b\lambda}, \quad m = \frac{I^2R_0}{2\pi b^2 lJ\lambda}, \quad \beta^2 = \mu^2 - m\alpha \text{ and } v = t - \frac{m}{\beta^2}$$

(1) reduces to $$\frac{d^2v}{dz^2} - \beta^2 v = 0$$

For $\beta^2 > O$ the solution of this equation is:—

$$t - \frac{m}{\beta^2} = A \sinh \beta z + B \cosh \beta z$$

where A and B are arbitrary constants. If the origin of z be placed at the middle of the wire the boundary conditions are $t = O$ at $z = \pm\, l$ whence, after evaluating A and B, we obtain:—

$$t = \frac{m}{\beta^2}\left(1 - \frac{\cosh \beta z}{\cosh \beta l}\right) \qquad (2)$$

giving the distribution of temperature along the wire.

For a sufficiently short and thick wire the distribution of temperature is very nearly parabolic, as can be seen by substituting the first two terms of the expansions for cosh βz and cosh βl. The parabolic distribution was assumed in the elementary theory previously given.

The mean temperature $\bar{t}$ along the wire is given by:—

$$\bar{t} = \frac{1}{2l}\int_{-l}^{+l} \frac{m}{\beta^2}\left(1 - \frac{\cosh \beta z}{\cosh \beta l}\right) dz$$

or $$\bar{t} = \frac{m}{\beta^2}\left(1 - \frac{\tanh \beta l}{\beta l}\right) \qquad (3)$$

If $\bar{R}$ is the observed resistance of the wire at the mean temperature $\bar{t}$ then $\bar{R} = R_0 (1 + \alpha \bar{t})$, giving

$$\bar{t} = \frac{\bar{R} - R_0}{R_0\, \alpha}.$$

(In actual experiments $\bar{t}$ is 3 or 4 degrees only.) Accordingly, on substituting for $\bar{t}$, (3) becomes:

$$\left(\frac{1}{\beta l}\right)^2 \left(1 - \frac{\tanh \beta l}{\beta l}\right) = \frac{2\pi b^2\lambda J(\bar{R} - R_0)}{R_0^2 I^2 \alpha l} \qquad (4)$$

(4) may be written in the form:

$$\frac{c}{\bar{R} - R_0} = \frac{\beta^3 l^3}{\beta l - \tanh \beta l}$$

where $$c = \frac{R_0^2 I^2 \alpha l}{2\pi b^2 J\lambda}$$

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Expanding tanh βl as a power series we obtain:

$$\frac{c}{\bar{R}-R_0} = \frac{\beta^3 l^3}{\beta l - (\beta l - \frac{1}{3}\beta^3 l^3 + 2/15\ \beta^5 l^5 - 17/315\ \beta^7 l^7 + \ldots)}$$

$$= 3\left[(1 + 2/5\ \beta^2 l^2) - \frac{\beta^4 l^4}{525}\right] \text{ (nearly)}$$

For values of βl not greater than unity, the error introduced in the right-hand side of the last equation by neglecting the term $\beta^4 l^4/525$ is small, e.g. for $\beta l = 1$ it is 1 in 300. If this term be neglected, we obtain, after simplification:

$$\frac{2h}{b\lambda} = \frac{R.I^2\alpha}{2\pi b^2 Jl}\left[\frac{5R_0}{6(\bar{R}-R_0)} + 1\right] - \frac{5\lambda}{2l^2} \tag{5}$$

If λ is known, (5) can be solved at once for h, and the conductivity k' of the gas obtained by multiplying h by the 'form factor' for radial flow between concentric cylinders, i.e.:—

$$k' = h \cdot b \log_e {}^a/_b.$$

where a is the inner radius of the tube.

The wires used in our experiments are not sufficiently short and thick for (5) to be applicable to the high conductivity gases, hydrogen, deuterium and helium. It is therefore necessary to solve the more general equation (4) for h. This is most conveniently done by tabulating the function:—

$$f = \left(\frac{1}{\beta l}\right)^2 \left(1 - \frac{\tanh \beta l}{\beta l}\right)$$

for different values of βl.

When the tube contains a high vacuum (pressure not greater than 10^{-5} mm. Hg.) the only lateral loss of heat from the wire is a very small one due to radiation, as the loss due to molecular conduction in the residual gas as shown below is negligible. If h_R be written for h in (5) this equation enables us to obtain the thermal conductivity λ of the wire since h_R may be obtained by calculation from radiation data. It is, however, more convenient for purposes of calculation to transform (5) into the equivalent form:—

$$\lambda = \frac{1}{6}\frac{\bar{R}R_0 l^2\ \alpha\ l}{\pi b^2 J(\bar{R}-R_0)}\left(1 + \frac{1}{30}\frac{R_0 l^2\ \alpha\ l}{\pi b^2\ J\lambda}\right)\left(1 - \frac{4}{5}\frac{h_R l^2}{b\lambda}\right) \tag{6}$$

This relation replaces the simpler relation (6) of Knudsen, given in the elementary theory. The quantites in the last two brackets on the right hand side of (6) represent small corrections only. It is therefore sufficient to use the approximate value of λ given by Knudsen's simple formula in evaluating them. The quantity h_R can be readily obtained. The radiation per cm.^{2} per second from a metal surface is:—

$$S = \epsilon\sigma T^4$$

where σ is Stefan's constant, T the absolute temperature, and ϵ the emissive power of the metal surface. It follows that:—

$$h_R = 4\epsilon\sigma T^3$$

The value of ϵ for a given metal can be obtained from experimental curves representing ϵ as a function of the wavelength. (The curves given in Geiger-Scheel, Handbuch der Physik, Vol. 21, p. 190, may be used.) The wavelength λ_{max} corresponding to a given temperature T can be obtained from Wien's Displacement Law :—

$$\lambda_{max} T = \cdot 288 \text{ cm. deg.}$$

The validity of (6) depends also on the heat transfer by molecular conduction in the high vacuum being negligible. It can be readily shown from a relation obtained by Knudsen (for which see Lorentz "Lectures on Theoretical Physics," vol. 1, p. 144) that the loss of heat per cm.^{2} per sec. from a wire at t°C to a coaxial surrounding cylinder at the temperature of 0°C which contains air at a pressure of p dyne cm.$^{-2}$ is :—

$$W < 3 \times 10^{-6}\, p \cdot t$$

This gives to the part h_c of h due to molecular conduction a value :—

$$h_c < 4 \times 10^{-7} \text{ cal. cm.}^{-2} \text{ sec.}^{-1} \text{ deg.}^{-1}$$

when the pressure is 10^{-4} mm. of mercury. Even at this pressure the effect of ignoring molecular conduction in (6) results in an error in λ of less than 1 part in 1000.

Exact Theory.

In the exact theory, for which we are indebted to Professor T. Cherry, the differential equation (1) must be replaced by the following differential equation holding at the surface of the wire :—

$$\lambda \pi b^2 \frac{\partial^2 t}{\partial z^2} + 2 \pi b k \left. \frac{\partial t}{\partial r} \right|_{r=b} + \frac{I^2 \rho_0}{J} (1 + \alpha t) = 0 \qquad (7)$$

where ρ_0 is the resistance of the wire per unit length. As before, the first two terms multiplied by dz represent the net rate of inflow of heat into the element dz along the wire and over its surface, while the last term multiplied by dz is the rate of generation of heat in dz by the electric current.

The solution of (7) is :—

$$t = \sum_n c_n \left[I_0 (nsr) / I_0 (nsa) - K_0 (nsr) / K_0(nsa) \right] \cos nsz$$

where $s = \pi / 2l$, (n being odd)

and $$\left. \frac{\partial t}{\partial r} \right|_{r=b} = \Sigma\, c_n\, ns \left[I_1 (nsb) / I_0 (nsa) - K_1 (nsb) / K_0 (nsa) \right] \cos nsz$$

$$= \Sigma\, c_n\, ns\, N_{1n} \cos nsz \text{ (say),}$$

and $$\left. \frac{\partial^2 t}{\partial z^2} \right|_{r=b} = - \Sigma\, c_n (ns)^2 \left[I_0 (nsb) / I_0 (nsa) - K_0 (nsb) / K_0 (nsa) \right] \cos nsz$$

$$= - \Sigma\, c_n (ns)^2 N_{0n} \cos nsz \text{ (say),}$$

and $t_{r=b} = \Sigma\, c_n N_{0n} \cos nsz.$

Also, for $-1 < z < +1$

$$I^2\rho_0/J = \left[4I^2\rho_0/J\pi\right]\left[\cos sz - \tfrac{1}{3}\cos 3sz + 1/5 \cos 5sz \ldots\ldots\right]$$

Hence, on substituting in (7) and equating coefficients of cos nsz we get:

$$c_n = \pm\left[2I^2R_0/nJ\pi l\right] \div \left[\lambda\pi b^2 (ns)^2 N_{0n} - 2\pi bk\,(ns)\,N_{1n} - I^2R_0\alpha N_{0n}/2Jl\right] \quad (8)$$

the sign being $+$ for $n = 1, 5, 9 \ldots$, and $-$ for $n = 3, 7, 11 \ldots$

The resistance of the whole wire from $z = -l$ to $z = +l$ is:

$$\bar{R} = \int_{-l}^{+l} \rho_0 (1 + \alpha\, t)dz = 2\rho_0 l + \left[4\rho_0 l\, \alpha/\pi\right]\left[c_1 N_{01} - \tfrac{1}{3} c_3 N_{03} + \tfrac{1}{5} c_5 N_{05} - \ldots\right]$$

or, since $R_0 = 2\,\rho_0\, l$

$$\pi(\bar{R} - R_0)\,/\,2R_0\alpha = c_1 N_{01} - \tfrac{1}{3} c_3 N_{03} + \tfrac{1}{5} c_5 N_{05} \ldots \quad (9)$$

where $N_{0n} = I_0\,(nsb)\,/\,I_0\,(nsa) - K_0\,(nsb)\,/\,K_0\,(nsa)$

The equations (8) and (9) together replace (4) of the approximate theory. It will be noticed that the thermal conductivity k of the gas occurs only in the co-efficients c_n defined by (8). The series on the right hand side of (9) converges very rapidly and the calculation of the first three terms allows k to be obtained by successive approximations. The expansions of the Bessel functions I_0, I_1 and K_0 are given in Whittaker and Watson, Modern Analysis, Chapter 17.

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